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(54) Title: CATALYTIC SYSTEM BASED ON BIMETALLIC CYANIDES AND THEIR USE IN THE SYNTHESIS OF POLYETHER-POLYOLS

(57) Abstract: A description follows of a catalytic system based on modified bimetallic cyanides (I), a method for their preparation and a process for the synthesis of polyether polyols which uses these catalysts. The method of preparing the catalysts comprises treating the catalyst precursor with a dehydrating agent.

CATALYTIC SYSTEM BASED ON BIMETALLIC CYANIDES AND THEIR USE IN THE SYNTHESIS OF POLYETHER-POLYOLS

The present invention relates to a catalytic system based on modified bimetallic cyanides, a process for their preparation and their use for the synthesis of polyether polyols.

Polyether polyols are extremely versatile compounds which can be used as such or as intermediates in the production of compounds of industrial interest such as polyurethanes, detergents or additives for oils.

These products are normally prepared by reacting an alkylene oxide, especially propylene oxide, ethylene oxide or their mixtures, with a compound having active hydrogen atoms (initiator) in the presence of a basic alkoxylation catalyst, in particular potassium hydroxide.

Although these catalysts allow polyether polyols to be produced with good properties, they

have a modest catalytic activity, and relatively long reaction times are therefore required to obtain a complete conversion of the alkylene oxide.

Another disadvantage is linked to the formation of unsaturated chain-end groups, due to secondary reactions induced by the alkalinity of the medium.

The use of catalytic systems based on metallic cyano-metallates, particularly zinc hexacyanoferrate and zinc hexacyanocobaltate (ZCC), has therefore been proposed in patent literature.

The preparation of these catalytic systems is effected by the reaction of a salt of a cyano-complex of a transition metal (for example potassium hexacyanocobaltate in the case of ZCC) with a metallic salt, for example zinc chloride, in an aqueous environment. The precipitate is washed with an aqueous solution of an organic compound to give the end-catalyst.

The catalysts obtained with this process however have a catalytic activity which is insufficient for industrial application as the presence in the catalyst of residual ionic species of the precursors causes its partial poisoning.

Alternative methods have therefore been pro-

posed for the preparation of catalysts with an improved catalytic activity.

U.S. patent 4,472,560, for example, describes the preparation of bimetallic cyanides modified by the addition of promoters such as zinc sulfate and hydrochloric acid.

U.S. patent 4,477,589 describes the synthesis of catalysts modified by the addition of zinc hydroxide (ZCCOH).

The document of Kuyper et al. J. of Catalysis **105**, 163-174 (1987) describes the preparation of catalysts modified with zinc chloride starting from the ZCCOH compound.

U.S. patent 5,998,327 describes the preparation of a ZCC catalyst modified with extremely poisonous cadmium salts.

U.S. patent 5,158,922 describes an improved process for the preparation of bimetallic cyanides which consists in controlling the process parameters such as the addition order of the solutions, the concentrations of the solutions and the excess of one with respect to the other, the temperature at which the precipitation occurs. The parameters are important for obtaining a reproducible high activity catalyst with reduced induction times.

U.S. patent 5,714,639 describes the preparation of a catalyst containing bimetallic cyanides consisting of a "paste" of these salts (10-60% by weight), an organic complexing agent (40-90% by weight) and water (1-20% by weight).

These catalysts produce amorphous, liquid polyether polyols with a suitable molecular weight and a low unsaturation degree. Their preparation however is extremely complex (Kuyper et al., 1987, J. Catal., **105**, 163) and the experimental parameters adopted in their preparation can substantially influence their catalytic activity. It has been observed in fact that in numerous cases even inert products are obtained.

These catalysts moreover have long and non-repro-ducible induction times which create problems relating to reaction control and plant safety.

Catalysts based on bimetallic cyanides characterized by a crystallinity lower than 30% have been prepared to overcome these specific safety problems (EP 654,302, U.S. 5,470,813 and EP 743,093).

Operating according to these processes, a reduction in the induction times in the polymerization of propylene oxide, has been observed. Although this reduction is significant, it is still

not satisfactory.

It has now been found that it is possible to overcome the drawbacks of the known art discussed above by means of a new class of catalysts based on modified bimetallic cyanides.

In particular the use of these catalysts allows the following advantages to be obtained: optimum catalytic activity, no induction time, good selectivity and preparation simplicity.

An objective of the present invention therefore relates to a new class of modified bimetallic (I) cyanides.

A further objective of the present invention relates to a process for the preparation of modified bimetallic (I) cyanides.

Yet another objective of the present invention relates to a process for the polymerization of epoxides which uses this modified catalytic system.

In particular, the new class of modified bimetallic catalysts according to the present invention has general formula (I)

$$M_a[M'[(CN)_r]_b X_c \cdot (Z)_d \qquad (I)$$

wherein: M represents an element selected from metals belonging to groups IB-VIIIB and IIIA-IVA, M' an element selected from transition metals of

groups IB-IIB and VB-VIIIB, Z is an oxygenated or nitrogenated organic compound and X a halogen; a, b c and r are integers depending on the valence state of the species; c can also be equal to zero; d has a value ranging from 0 to 12.

Examples of metals M are zinc, aluminum, zirconium, titanium, iron, lanthanides. Zinc is preferred.

Examples of metals M' are cobalt, iron, chromium, nickel. Cobalt and iron are preferred.

The Z compounds are selected from groups of ethers, esters, ketones, amides, nitriles or carbonates.

Examples of Z compounds are dimethyl ether, diethyl ether, diisopropyl ether, di-tert-butyl ether, dimethoxyethane, diethylene glycol, tetrahydrofuran, acetonitrile, dimethylcarbonate, di-t-butyl carbonate, polyether-polyols with a molecular weight < 600, dioxane, anisole, acetone or methyl ethyl ketone.

The catalyst having formula (I) is obtained by means of a process which comprises:

(a) synthesizing a catalyst having formula (II)

$$M_a[M'[(CN)_r]_b\ (OH)_{c'}\ (H_2O)_f\ (Z)_{d'} \qquad (II)$$

wherein: M, M', Z, a, r, b, c have the same mean-

ings defined above, f and d' are coefficients whose sum ranges from 1 to 15;

(b) treating the catalyst (II) with a dehydrating agent having general formula (III)

$$A(O)_gX'_h \qquad (III)$$

wherein: A is an element selected from boron, sulfur, phosphorous and carbon, X' is a halogen or an alkoxyl group, g and h are integer coefficients depending on the oxidation state of A, g may also be 0;

in the presence of an oxygenated or nitrogenated liquid organic complexing agent Z having the same meaning defined above.

Examples of dehydrating agents (III) suitable for the purposes of the present invention are thionyl chloride, phosgene, sulfuryl chloride, phosphorous pentachloride, phosphorous trichloride, boron trichloride and the corresponding bromides, dimethylcarbonate, di-t-butyl carbonate, dimethylsulfate.

Thionyl chloride, thionyl bromide, phosgene are preferred as they produce reaction by-products which can be easily removed from the end-product.

Complexing agents suitable for the purposes of the present invention are selected from dimethyl

ether, diethyl ether, diisopropyl ether, di-tert-butyl ether, dimethoxyethane, diethyleneglycol, tetrahydrofuran, acetonitrile, dimethylcarbonate, di-t-butyl carbonate, polyether-polyols with a molecular weight < 600, dioxane, anisole, acetone or methyl ethyl ketone.

The treatment is effected by adding the dehydrating agent to a suspension of the catalyst having formula (II) in the complexing agent at a temperature ranging from 0°C to the boiling point of the solvent, for a time ranging from 30 minutes to 24 hours.

At the end of the treatment, the solid product is recovered by the conventional techniques.

The content of complexing agent in the catalyst was determined by means of extraction with acetone and gaschromatographic analysis of the solution.

The selectivity of the catalyst, intended as capacity of limiting the formation of chain-end double bonds, is indicated by the relative content of unsaturated groups with respect to that of hydroxyl groups; these values are determined by polarographic and potentiometric titration respectively.

The catalyst of the present invention is active in synthesis processes of polyether polyols by the reaction of an alkylene oxide with one or more compounds, indicated by the term initiators, capable of promoting the formation of hydroxy-alcohol chain-end groups.

The alkylene oxides are selected from epichlorohydrin, propylene oxide, ethylene oxide, butene oxide or their mixtures.

The quantity of oxide used in the process is selected in relation to the molecular weight which is desired for obtaining the polyether polyols.

The initiators are water or polyfunctional alcohols with from 2 to 20 carbon atoms, in particular from 2 to 10 carbon atoms, or polyols with a molecular weight lower than 1,000 daltons.

Examples of initiators are: glycols such as for example, ethylene, propylene, butylene glycol; diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, cyclohexanediol, cyclohexanedimethanol, benzenedimethanol, aromatic diols such as hydroquinone, methylhydroquinone, catechol, resorcinol, naphthalenediol, dihydroxybiphenyl; aliphatic polyfunctional alcohols such as glycerin, pentaerythritol, trimethylolpropane or aromatic such as

for example pyrogallic acid; sugar derivatives (pentose or hexose) such as sorbitol, mannitol, glucitol, xylitol, ribitol, etc.

Alternatively, polyfunctional acids can also be used such as succinic, glutaric, malonic, adipic acid or hydroxy-acids such as hydroxyacetic, hydroxypropionic, hydroxybutanoic, hydroxyhexanoic, hydroxybenzoic, citric, tartaric acid. Finally, polyfunctional amines can also be used, such as ethylenediamine, tetramethylenediamine, hexamethylenediamine, isophoron-diamine, benzenediamine, diaminobiphenyl, etc.

The selection of the suitable initiator also depends on the polymer to be prepared.

Bifunctional initiators, for example, are particularly suitable for the preparation of polyether polyols which can be used for the production of polyurethane elastomers.

The quantity of catalyst used can vary within wide limits. A quantity of catalyst ranging from 10^{-2} to 10^{-6} grams per gram of monomer, preferably from 10^{-3} to 10^{-5} grams per gram of monomer, is generally used.

The polymerization can be carried out in the absence or in the presence of a hydrocarbon solvent

such as, for example pentane, hexane, heptane, cyclohexane, toluene, benzene, xylene, ethylbenzene, cumene or an ether solvent such as ethyl ether, propyl ether, isopropyl ether, butyl ether, tetrahydrofuran, pyran, dioxane, dimethoxyethane, dimethoxypropane, dimethoxybutane or diethoxyethane.

The temperatures used in the process of the present invention generally range from 50°C to 180°C, preferably from 80°C to 120°C. The reaction is normally carried out in a closed system, at a pressure which generally does not exceed 8 Bar, preferably 6 Bar.

After the polymerization is complete, the catalyst can be removed from the product by the conventional techniques, such as filtration, for example.

The process of the present invention can be carried out batchwise or in continuous.

The polyols obtained with the process of the present invention were characterized by means of nuclear magnetic resonance spectroscopy to determine the degree of stereoregularity and by means of scan differential calorimetry to identify the melting point. The products proved to be liquid, and therefore without a melting point. NMR analysis

demonstrated that the products were not stereoregular (atactic).

The following examples have the sole purpose of describing the present invention in greater detail and should in no way be considered as limiting its scope.

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EXAMPLE 1

Preparation of the catalyst A

A solution of 22.89 g of potassium hexacyanocobaltate [$K_3Co(CN)_6$] in 495 ml of water is charged, at room temperature and at a rate of 2.7 ml/minute, into a 1 liter beaker containing a solution of 20.41 g of zinc chloride in 175 ml of distilled water.

A solution of 2.8 g of sodium hydroxide in 200 ml of water is added to the resulting mixture at a rate of 2.5 ml/minute. The solid obtained is filtered, washed with distilled water (500 ml x 5 times) and dried in an oven at 50°C until the weight is constant.

The presence of water molecules in the solid obtained $Zn_2[Co(CN)_6]OH{\cdot}13H_2O$ is confirmed by IR analysis.

2 g of the product obtained above and 10 ml of

1,2-dimethoxyethane are introduced into a test-tube, in a nitrogen atmosphere. 4 ml of thionyl chloride are slowly added to the container, immersed in a water and ice bath. After 30 minutes the bath is removed and after a further 4.5 hours under stirring at room temperature, the product is filtered under nitrogen, washed with anhydrous toluene and dried under vacuum for 5 hours.

Upon IR analysis the resulting product appears to be free of crystallization water, whereas it shows the characteristic band of complexed dimethoxyethane at 1055 cm^{-1} (C-O-C asymm. stretching) and 860 cm^{-1} (C-O-C symm. stretching).

The X-ray spectrum (figure 1) does not correspond to any published structure. The product, which is at least 90% crystalline, has a face centered cubic (FCC) symmetry. The structure of the compound in question was calculated with the relative parameters. X-ray data processing also confirms the total absence of crystallization water.
Elemental analysis data: Zn = 26.2%, Co = 13.4%
Organic component content (dimethoxyethane): 13.4%.

1.016 g of this product are subsequently suspended in an inert atmosphere in 19 g of polypropyleneglycol (MW = 425) previously treated by per-

colation on a basic alumina bed and conserved on activated molecular sieves.

EXAMPLE 2

Preparation of catalyst B

A solution of 2.125 g of potassium hexacyano-cobaltate [$K_3Co(CN)_6$] in 45.9 ml of water is added dropwise, in about 10 minutes, to a solution of zinc chloride (1.306 g) in 11.2 ml of distilled water.

The precipitate is filtered, washed 4 times with 50 ml of distilled water and filtered each time. At the end of the operation, the solid is dried in an oven at 60°C for 16 hours.

1 g of this product and 10 ml of 1,2-dimethoxyethane are introduced into a test-tube in a nitrogen atmosphere.

The container is immersed in a water and ice bath and 1.3 ml of thionyl chloride slowly added. After 30 minutes the bath is removed and, after a further 1.5 hours under stirring at room temperature, the product is filtered under nitrogen, washed with anhydrous toluene and dried under vacuum for 5 hours.

Upon IR analysis the resulting product appears to be free of crystallization water, whereas it

shows the characteristic band of complexed dimethoxyethane at 1055 cm^{-1} (C-O-C asymm. stretching) and 869 cm^{-1} (C-O-C symm. stretching). The X-ray spectrum is indicated in figure 2 and does not correspond to any known species.

Elemental analysis data: Zn = 22.8%, Co = 13.3%

Organic component content (dimethoxyethane): 18%.

501 mg of this product are suspended in an inert atmosphere in 9.5 g of polypropyleneglycol previously treated by percolation on a basic alumina bed and conserved on activated molecular sieves.

EXAMPLE 3

Preparation of catalyst C

A solution of 22.89 g of potassium hexacyanocobaltate [$K_3Co(CN)_6$] in 495 ml of water is charged, at room temperature and at a rate of 2.7 ml/minute, into a 1 liter beaker containing a solution of 20.41 g of zinc chloride in 175 ml of distilled water.

A solution of 2.8 g of sodium hydroxide in 200 ml of water is added to the resulting mixture at a rate of 2.5 ml/minute. The solid obtained is filtered, washed with distilled water (500 ml x 5 times) and dried in an oven at 50°C until the weight is constant.

The presence of water molecules in the solid obtained $Zn_2[Co(CN)_6]OH \cdot 13H_2O$ is confirmed by IR analysis.

3 g of the product obtained above and 12 ml of acetonitrile are introduced into a test-tube in a nitrogen atmosphere. The container is immersed in a bath at 16°C and 6 ml of thionyl chloride are subsequently slowly added. After 30 minutes the bath is removed and after a further 1.5 hours under stirring at room temperature, the product is filtered under nitrogen, washed with anhydrous toluene and dried under vacuum for 24 hours.

Upon IR analysis the resulting product appears to be free of crystallization water, whereas it shows the characteristic band of complexed acetonitrile at 2322 cm^{-1} and 2295 cm^{-1} (CN stretching).

Elemental analysis data: Zn = 29.1%, Co = 15.9%

Organic component content (acetonitrile): 10.1%.

EXAMPLE 4

Preparation of catalyst D

The procedure of example 1 was repeated, except for the fact that at the end 0.624 g of solid catalyst were suspended in an inert atmosphere in 7.9 g of glycerol propoxylate (molecular weight 260) previously anhydrified by contact with acti-

vated molecular sieves.

EXAMPLE 5

Preparation of catalyst E

A solution of 4.250 g of potassium hexacyanocobaltate [$K_3Co(CN)_6$] in 90 ml of water is added dropwise, in about 20 minutes, to a solution of zinc chloride (2.605 g) in 22.5 ml of distilled water.

The precipitate is filtered, washed 4 times with 80 ml of distilled water and filtered each time. At the end of the operation, the solid is dried in an oven at 60°C for 16 hours.

3 g of this product are reacted in a nitrogen atmosphere with 15 ml of dimethyl carbonate at 50°C for 7 hours. The product is then filtered under nitrogen and dried under vacuum for 5 hours.

Upon IR analysis the resulting product appears to be free of crystallization water, whereas it shows characteristic bands of complexed dimethyl carbonate at 1667 cm^{-1} (C=O stretching) and 1331 cm^{-1} (O-C-O asymm. stretching).

Elemental analysis data: Zn = 22.2%, Co = 13.3%

Organic component content (dimethyl carbonate): 18.2%.

1.004 g of this product are suspended in an

inert atmosphere in 19.1 g of polypropyleneglycol previously treated by percolation on a basic alumina bed and conserved on activated molecular sieves.

EXAMPLE 6

Preparation of catalyst F

A solution of 2.125 g of potassium hexacyanocobaltate [$K_3Co(CN)_6$] in 45.5 ml of water is added dropwise, in about 10 minutes, to a solution of zinc chloride (1.305 g) in 11.5 ml of distilled water.

The precipitate is filtered, washed 4 times with 50 ml of distilled water and filtered each time. At the end of the operation, the solid is dried in an oven at 60°C for 16 hours.

2 g of this product are reacted in a nitrogen atmosphere with 30 ml of di-t-butyl carbonate at 55°C for 6 hours. The product is then filtered under nitrogen and dried under vacuum for 16 hours.

Upon IR analysis the resulting product appears to be free of crystallization water, whereas it shows the characteristic band of complexed di-t-butyl carbonate at 1669 cm^{-1} (C=O stretching) and 1345 cm^{-1} (O-C-O asymmetrical stretching).

Elemental analysis data: Zn = 22.0%, Co = 12.9%

Organic component content (di-t-butyl carbonate): 19.1%.

990 mg of this product are suspended in an inert atmosphere in 19 g of polypropyleneglycol previously treated by percolation on a basic alumina bed and conserved on activated molecular sieves.

EXAMPLE 7

Synthesis of polyether polyols

1 g of catalyst A, removed and weighed in an inert atmosphere, and 10 ml of propylene oxide (PO) in an inert atmosphere are charged into a 25 ml reactor, equipped with a magnetic stirrer and heat exchanger (oil bath). The reaction is carried out at 80°C for 4 hours. The pressure in the reactor does not exceed 3.5 atmospheres. The non-reacted PO is removed from the reaction mixture under reduced pressure conditions.

8.1 g of polyol are obtained, corresponding to an 83% conversion with respect to the monomer used.

The polyol thus obtained is diluted with 100 ml of acetone, filtered on a layer of celite to separate the catalyst and is then subjected to a pressure of 0.001 Bar to evaporate the solvent.

Double bond content: 0.0043 mmoles/g

Hydroxyl content: 41 mg KOH/g

EXAMPLE 8

Synthesis of polyether polyols

The reaction is carried out under the same conditions indicated in example 7, but using 0.5 g of catalyst A and adding 0.5 g of anhydrous poly-proyleneglycol.

8.6 g of polyol are obtained, corresponding to a 92% conversion.

Double bond content: 0.0043 mmoles/g

Hydroxyl content: 22 mg KOH/g

EXAMPLE 9

Synthesis of polyether polyols

The reaction is carried out under the same conditions indicated in example 8, but bringing the temperature to 25°C after 4 hours and adding a further 10 ml of propylene oxide in an inert atmosphere.

10.3 g of polyol are obtained, corresponding to a total conversion of 57%.

Double bond content: 0.0125 mmoles/g

EXAMPLE 10

Synthesis of polyether polyols

The same procedure is adopted as described in

example 8, but carrying out the reaction at 100°C.

7.1 g of polyol are obtained, corresponding to a total conversion of 73%.

Double bond content: 0.013 mmoles/g

Hydroxyl content: 58 mg KOH/g

EXAMPLE 11

Synthesis of polyether polyols

The reaction is carried out under the same conditions indicated in example 7, but using catalyst B.

8.09 g of polyol are obtained, corresponding to a conversion of 86%.

Double bond content: 0.0077 mmoles/g

Hydroxyl content: 31 mg KOH/g

EXAMPLE 12

Synthesis of polyether-polyol

0.7 g of catalyst D are used in a polymerization procedure analogous to that described in example 7.

6.95 g of polyol are obtained, corresponding to a conversion of 76%.

Double bond content: 0.0088 mmoles/g

Hydroxyl content: 58 mg KOH/g

EXAMPLE 13

Synthesis of polyether-polyol

0.54 g of catalyst C, removed and weighed in an inert atmosphere, suspended in 0.50 g of polypropyleneglycol (MW ≈ 400), and 10 ml of propylene oxide (PO) in an inert atmosphere are charged into a 25 ml reactor, equipped with a magnetic stirrer and heat exchanger (oil bath). The reaction is carried out at 80°C for 4 hours. The pressure in the reactor does not exceed 3.5 Bar. The non-reacted PO is removed from the reaction mixture under reduced pressure conditions.

1.71 g of polyol are obtained, corresponding to a conversion of 14.6% with respect to the monomer used.

A further 10 ml of propylene are added to the product thus obtained. After 4 hours of reaction at 80°C, and after evaporation under vacuum of the non-reacted monomer, 3.0 g of polyol are recovered, equal to an additional conversion of 15.5% in the second reaction phase.

Double bond content: 0.0068 mmoles/g

Hydroxyl content: 52 mg KOH/g

<u>EXAMPLE 14 (comparative)</u>

A catalyst is prepared according to the procedure described in J. of Catalysis **105**, 163-174 (1987).

A solution of 5.73 g of potassium hexacyanocobaltate in 123.75 g of distilled water is added at a rate of 2.5 ml/minute to a solution of zinc chloride (5.1 g) in 43.74 g of distilled water.

A solution of 0.7 g of sodium hydroxide in 50 g of distilled water is added to the resulting mixture, at a rate of 2.5 ml/minute.

The precipitate is filtered, washed 5 times with 65 ml of distilled water and filtered each time.

A portion of the solid is dried at 50°C until the weight is constant.

The presence of water molecules in the solid obtained $Zn_2[Co(CN)_6]OH \cdot 13H_2O$ is confirmed by IR analysis.

The wet solid is suspended in 15.1 g of dimethoxyethane and 5.4 g of a solution consisting of 5.07 g of hydrochloric acid and 7.45 g of distilled water are added to the suspension. The suspension is kept under light stirring for a night.

At the end of this period, 3 g of a solution of zinc sulfate (2.16 g) in 3.84 g of distilled water are added. The mixture thus obtained is kept at room temperature for two days and is then suspended in 65 g of polypropyleneglycol (PPG 400). The sus-

pension obtained is treated for 2 hours at 0.001 atmospheres at 50°C. IR analysis of the compound showed the presence of characteristics water bands.

EXAMPLE 15 (comparative)

1 g of catalyst prepared as described in example 14, removed and weighed in an inert atmosphere, and 10 ml of propylene oxide (PO) in a nitrogen atmosphere are charged into a 25 ml reactor, equipped with a mechanical stirrer and immersed in an oil bath. The reaction is carried out at 80°C for 4 hours. After 35 minutes the pressure inside the reactor suddenly rises to above 10 atmospheres, causing the safety valve to open. At the end of 4 hours, the non-reacted PO is removed from the reaction mixture under reduced pressure conditions.

6.6 g of polyol are obtained, corresponding to a conversion of 67%.

The polyol thus obtained is diluted in 100 ml of acetone, filtered on a layer of celite to separate the catalyst and is then subjected to a pressure of 0.001 Bar to evaporate the solvent.

Double bond content: 0.024 mmoles/g

Hydroxyl content: 77 mg KOH/g

EXAMPLE 16 (comparative)

The same procedure is adopted as described in

example 10, but carrying out the reaction at 65°C.

6.1 g of polyol are obtained, corresponding to a conversion of 64%.

The polyol thus obtained is diluted in 100 ml of acetone, filtered on a layer of celite to separate the catalyst and is then subjected to a pressure of 0.001 Bar to evaporate the solvent.

Double bond content: 0.0087 mmoles/g

Hydroxyl content: 82 mg KOH/g

EXAMPLE 17 (comparative)

A catalyst is prepared using the same procedure described in U.S. patent 5,714,639.

302 g of distilled water, 7.4 g of potassium hexacyanocobaltate and 39 g of ter-butanol are charged into a 500 ml flask equipped with a mechanical stirrer, drip funnel and thermometer. The mixture is stirred until the complete dissolution of the cobalt *salt and is then heated to 30°C for 30 minutes.*

A solution of $ZnCl_2$ (76 g) in 76 g of distilled water is then dripped into the flask maintained at 30°C, in about 25 minutes.

The end-suspension is centrifuged, suspended under vigorous mechanical stirring in a solution of 102 g of ter-butanol in 56 g of distilled water and

kept under stirring for 30 minutes.

The suspension is centrifuged again, resuspended under vigorous mechanical stirring in a solution of 143 g of ter-butanol in 1 liter of distilled water and kept under stirring for 30 minutes. The suspension is centrifuged obtaining 20 g of catalyst.

EXAMPLE 18 *(comparative)*

0.204 g of catalyst prepared as described in example 17, removed and weighed in an inert atmosphere, 0.809 g of PPG 400 and 10 ml of propylene oxide in an inert atmosphere at 80°C, are charged into a 25 ml reactor, equipped with a mechanical stirrer and immersed in an oil bath. After 5 minutes of reaction, the pressure inside the reactor suddenly rises to above 10 atmospheres, causing the safety valve to open. At the end of 4 hours, the non-reacted PO is removed from the reaction mixture under reduced pressure conditions.

7.9 g of polyol are obtained, corresponding to a conversion of 81%.

Double bond content: 0.012 mmoles/g

CLAIMS

1. A catalyst having general formula (I)

$$M_a[M'[(CN)_r]_bX_c \cdot (Z)_d \quad (I)$$

wherein: M represents an element selected from metals belonging to groups IB-VIIIB and IIIA-IVA, M' an element selected from transition metals of groups IB-IIB and VB-VIIIB, Z is an oxygenated or nitrogenated organic compound and X a halogen; a, b c and r are integers depending on the valence state of the species; c can also be equal to zero; d has a value ranging from 0 to 12.

2. The catalyst according to claim 1, wherein M is selected from zinc, aluminum, zirconium, titanium, iron and lanthanides.

3. The catalyst according to claim 2, wherein M is zinc.

4. The catalyst according to claim 1, wherein M' is selected from cobalt, iron, chromium and nickel.

5. The catalyst according to claim 4, wherein M' is cobalt or iron.

6. The catalyst according to claim 1, wherein Z

is selected from groups of ethers, esters, ketones, amides, nitriles or carbonates.

7. The catalyst according to claim 6, wherein Z is selected from dimethyl ether; diethyl ether, diisopropyl ether, di-tert-butyl ether, dimethoxyethane, diethyleneglycol, tetrahydrofuran, acetonitrile, dimethylcarbonate, di-t-butyl carbonate, polyether-polyols with a molecular weight < 600, dioxane, anisole, acetone or methyl ethyl ketone.

8. A method for the preparation of a catalyst having general formula (I) which comprises:

(a) synthesizing a catalyst having formula (II)

$$M_a[M'[(CN)_r]_b\ (OH)_c\ (H_2O)_f\ (Z)_{d'} \qquad (II)$$

wherein: M, M', Z, a, r, b, c have the same meanings defined above, f and d' are coefficients whose sum ranges from 1 to 15;

(b) treating the catalyst (II) with a dehydrating agent having general formula (III)

$$A(O)_g X'_h \qquad (III)$$

wherein: A is an element selected from boron, sulfur, phosphorous and carbon, X' is a halogen or an alkoxyl group, g and h are integer coefficients depending on the oxidation state

of A, g may also be 0;

in the presence of an oxygenated or nitrogenated liquid organic complexing agent Z.

9. The method according to claim 8, wherein the dehydrating agent (III) is selected from thionyl chloride, phosgene, sulfuryl chloride, phosphorous pentachloride, phosphorous trichloride, boron trichloride and the corresponding bromides, dimethylcarbonate, di-t-butyl carbonate and dimethylsulfate.

10. The method according to claim 9, wherein the dehydrating agent (III) is selected from thionyl chloride, thionyl bromide, dimethyl carbonate, di-t-butyl carbonate and phosgene.

11. The method according to claim 8, wherein the complexing agent is selected from the groups of ethers, esters, ketones, amides, nitriles or carbonates.

12. The method according to claim 11, wherein the complexing agent is selected from dimethyl ether, diethyl ether, diisopropyl ether, di-tert-butyl ether, dimethoxyethane, diethyleneglycol, tetrahydrofuran, acetonitrile, dimethylcarbonate, di-t-butyl carbonate, polyether-polyols with a molecular weight < 600,

dioxane, anisole, acetone or methyl ethyl ketone.

13. The method according to claim 8, wherein the treatment in step (b) is effected at a temperature ranging from 0°C to the boiling point of the solvent, for a time ranging from 30 minutes to 24 hours.

14. A process for the preparation of polyether polyols by the reaction of an alkylene oxide with one or more compounds capable of promoting the formation of hydroxy-alcohol chain-end groups, in the presence of a catalyst, wherein said process is characterized in that the catalyst is a compound having formula (I)

$$M_a[M'[(CN)_r]_bX_c \cdot (Z)_d \qquad (I)$$

wherein: M, M', Z, X and a, b, c and r have the meaning defined above.

15. The process according to claim 14, wherein the alkylene oxide is selected from epichlorohydrin, propylene oxide, ethylene oxide, butene oxide or their mixtures.

16. The process according to claim 14, wherein the compound capable of promoting the formation of hydroxy-alcohol chain-end groups, is selected from water, polyfunctional alcohols having

from 2 to 20 carbon atoms, polyols with a molecular weight lower than 1,000 daltons, polyfunctional acids, hydroxy-acids or polyfunctional amines.

17. The process according to claim 16, wherein the polyfunctional alcohols have from 2 to 10 carbon atoms.

18. The process according to claim 17, wherein the alcohols are selected from glycols, diols, aromatic diols, aliphatic or aromatic polyfunctional alcohols and pentose or hexose sugar derivatives.

19. The process according to claim 18, wherein the glycols are selected from ethylene, propylene, butylene glycol.

20. The process according to claim 18, wherein the diols are selected from 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, cyclohexanediol, cyclohexanedimethanol, benzenedimethanol, hydroquinone, methylhydroquinone, catechol, resorcinol, naphthalenediol, dihydroxybiphenyl.

21. The process according to claim 18, wherein the alcohols are selected from glycerin, pentaerythritol, trimethylolpropane or pyrogallic acid.

22. The process according to claim 18, wherein the sugar derivatives are selected from sorbitol, mannitol, glucitol, xylitol and ribitol.

23. The process according to claim 16, wherein the polyfunctional acids are selected from succinic, glutaric, malonic, adipic acid.

24. The process according to claim 16, wherein the hydroxyacids are selected from hydroxyacetic, hydroxypropionic, hydroxybutanoic, hydroxyhexanoic, hydroxybenzoic, citric, tartaric acid.

25. The process according to claim 16, wherein the polyfunctional amines are selected from ethylenediamine, tetramethylenediamine, hexamethylenediamine, isophoron-diamine, benzenediamine, diaminobiphenyl.

26. The process according to claim 14, wherein the quantity of catalyst (I) ranges from 10^{-2} to 10^{-6} grams per gram of monomer.

27. The process according to claim 26, wherein the quantity of catalyst (I) ranges from 10^{-3} to 10^{-5} grams per gram of monomer.

28. The process according to claim 14, wherein the polymerization reaction is carried out at a temperature ranging from 50°C to 180°C.

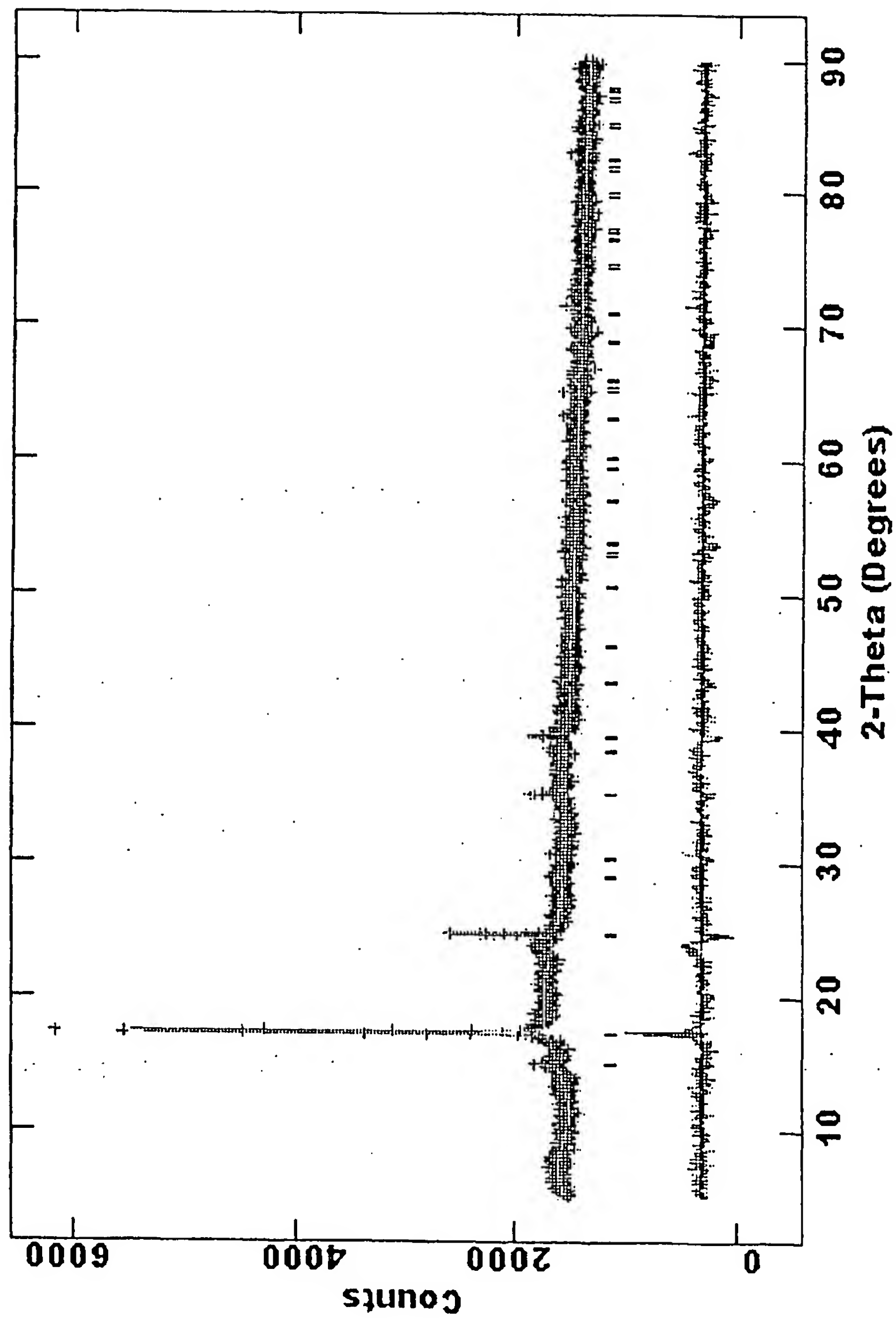
29. The process according to claim 28, wherein the temperature ranges from 80°C to 120°C.

30. The process according to claim 14, wherein the polymerization reaction is carried out at a pressure not higher than 8 Bar.

31. The process according to claim 30, wherein the polymerization reaction is carried out at a pressure not higher than 6 Bar.

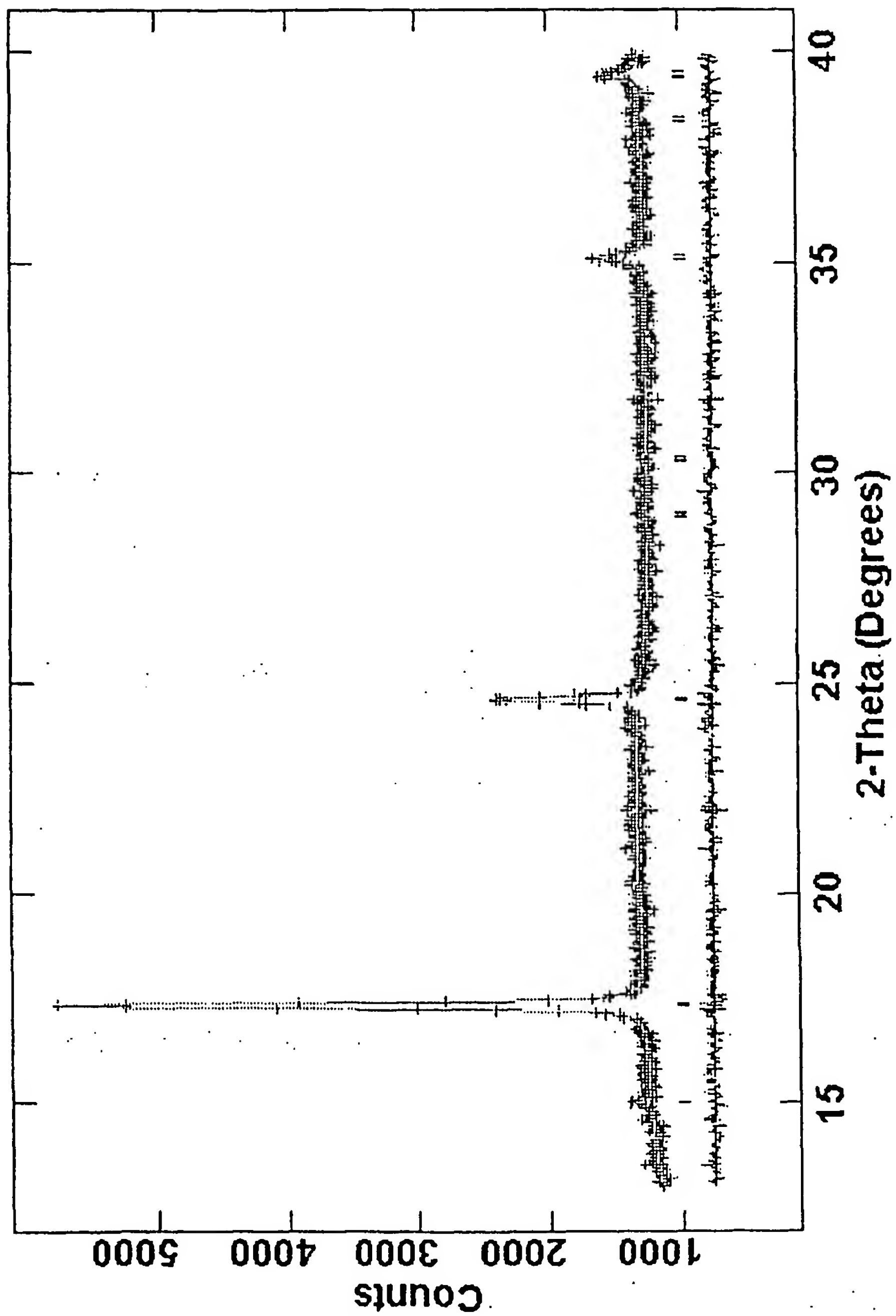
32. The process according to claim 14, wherein the polymerization is carried out in the presence of a hydrocarbon solvent selected from pentane, hexane, heptane, cyclohexane, toluene, benzene, xylene, ethylbenzene, cumene or ether solvent such as ethyl, propyl, isopropyl, butyl ether, tetrahydrofuran, pyran, dioxane, dimethoxyethane, dimethoxypropane, dimethoxybutane or diethoxyethane.

Fig.1



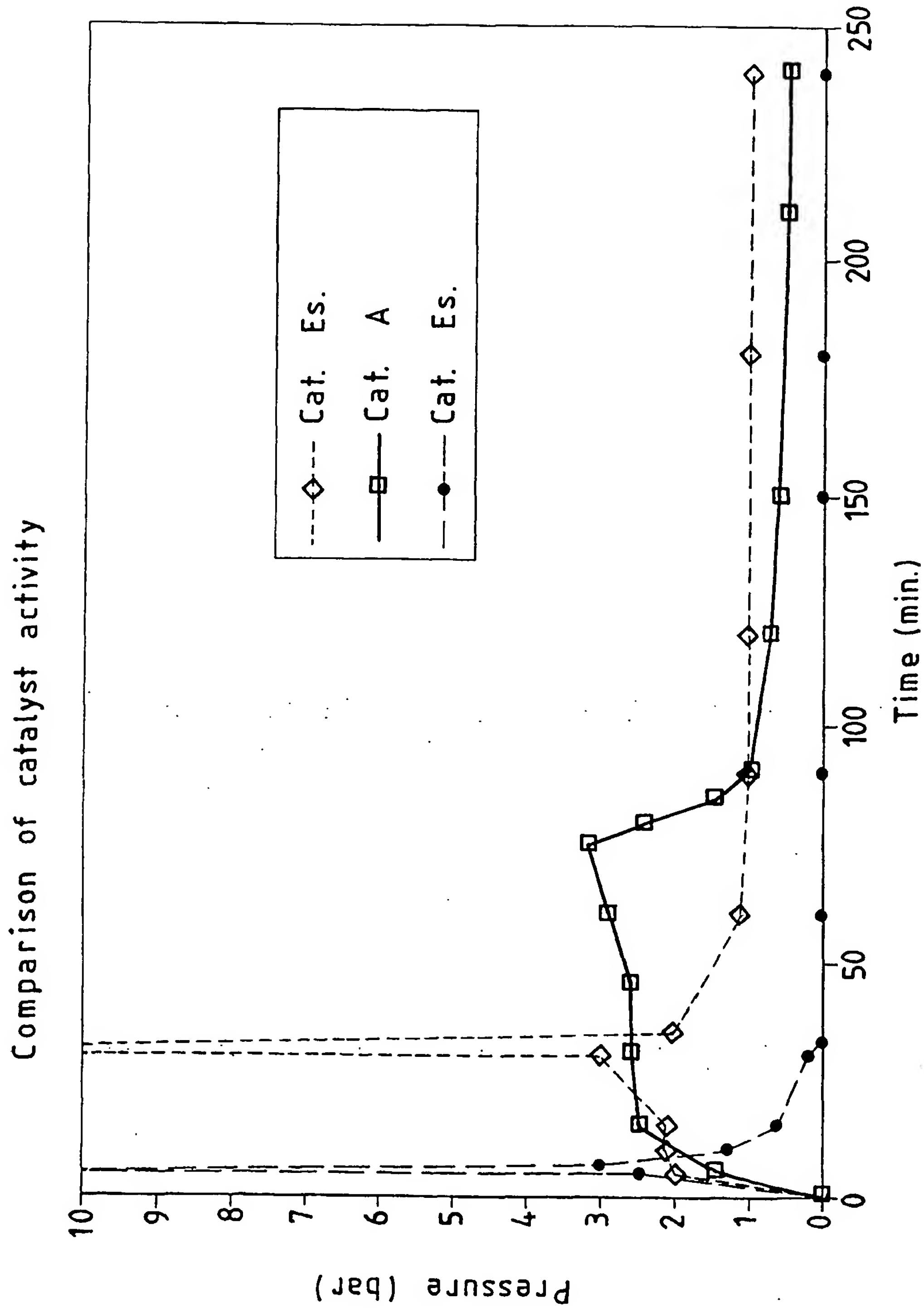
Powder XRD profile - calculated, observed and their difference

Fig.2



Powder XRD profile - calculated, observed and their Difference

Fig.3


Comparison of catalyst activity
Cat. Es.
Cat. A
Cat. Es.
Pressure (bar)
Time (min.)
0
1
2
3
4
5
6
7
8
9
10
0
50
100
150
200
250

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/05247

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J27/26 C08G65/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, API Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 998 672 A (LE-KHAC BI ET AL) 7 December 1999 (1999-12-07) abstract column 6, line 13 - line 63; examples 1,2	1-7, 14-32
X	GB 1 063 526 A (GEN TIRE & RUBBER CO) 30 March 1967 (1967-03-30) claims 1,2,4,5,12,17,18; examples 10,12,15,18	1-7, 14-32
A	US 5 998 327 A (PIELARTZIK HARALD ET AL) 7 December 1999 (1999-12-07) cited in the application column 5, line 53 -column 6, line 12	14-32

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 August 2001	22/08/2001

Name and mailing address of the ISA	Authorized officer
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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-32 (in part)

The wording of independent claims 1,8 and 14 is such that a lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. In particular, it is not clear which ranges of metals are defined by M and M'. It is not clear which notation (new IUPAC, old IUPAC, CAS, other?) is used to indicate the groups in the periodic table. As a result it cannot be determined which compounds for which compounds protection is sought.

In addition, present claims 1-32 seem to relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds in which M is zinc and M' is cobalt or iron.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP 01/05247

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